High Pressure Cell for Simultaneous Synchrotron Small-Angle X-ray Scattering and Laser Light Scattering Measurements

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With increasing temperature and pressure beyond its critical point, a one-component fluid can have its density approaching that of a corresponding liquid and acquire solvent properties much like those of liquids. Such fluids are known as "supercritical fluids". By varying the external parameters of temperature and pressure, one can control the interactions between the polymer and the fluid environment. A number of high pressure cells have been constructed for scattering measurements in supercritical carbon dioxide, $scCO_2$. However, none of the reported high pressure cells had the capacity to provide scattering measurements using more than one probe radiation simultaneously. In order to obtain the scattering information covering a wide *q*-range, we have developed a temperature and pressure controlled chamber for simultaneous SAXS and light scattering (LS) measurements.

The cell has two perpendicular scattering planes. Two diamond windows were used as the windows for the x-ray beams and five sapphire windows were installed at 0°, 35°, 90°, 145°, and 180° for transmitting the incident laser beam and for receiving the scattered light. The cell had a volume of 3.6 mL and a maximum pressure rating of 700 bar. A 4 mm x 12 mm Teflon-coated magnetic stirring bar was placed directly in the cell, so that the solution could be stirred while the cell was positioned in the beam. The block copolymer used in this study was poly(2-tetrahydropyranyl methacrylate)-b-poly(1H,1H-perfluorooctyl methacrylate) (THPMA-b-F7MA). THPMA-b-F7MA has an overall number-average molecular weight M_n of 7.7 x 10^3, with a polydispersity index M_w/M_n = 1.08, and a volume fraction of fluorinated block (F7MA) of 0.77. SAXS measurements were performed at the SUNY X27C beamline of the NSLS.

Figure 1 shows the representative SAXS profiles for the THPMA-*b*-F7MA in CO_2 at C = 18 mg/mL and T = 52 °C as a function of pressure. Below P = 121 bar, no excess scattered intensity was detected, indicating that the copolymer did not dissolve in $scCO_2$ at low pressures. From the figure we can see that the scattered intensity across the entire *q*-range increased drastically with increasing pressure from 121 bar to 217 bar. However, upon further increase in pressure, the scattered intensity decreased and finally, the shape of the SAXS curves at P = 480 bar was almost the same as that observed at P = 121 bar, except for the absolute scattered intensity. Thus, two different regimes were evident for the THPMA-*b*-F7MA solution in CO_2: (1) at low and high pressures, the scattered intensity was low and the shape of the SAXS profiles showed a very weak *q*-dependence, indicating that scattering originated from unassociated block copolymer chains, denoted as unimers. (2) At intermediate pressures, the scattered intensity increased drastically in the low *q*-region, indicating an association of unimers into micelles. According to Gunier plots, the micelles with $R_g = 3 \pm 0.1$ nm existed in $scCO_2$ at intermediate pressures.

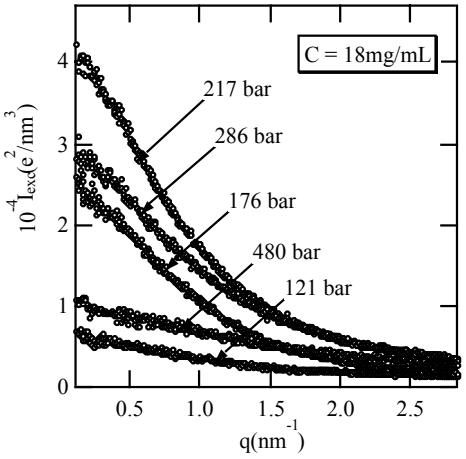

Fig. 1. Pressure dependence of corrected SAXS profiles of 18 mg/mL THPMA-*b*-F7MA diblock copolymer solution in $scCO_2$ at T = 52 °C.

The phase behaviors of THPMA-*b*-F7MA solution in CO_2 were also investigated by using dynamic light scattering (DLS) measurements. At intermediate pressures, two species with different size were coexisted in $scCO_2$, corresponding to unimers and micelles, respectively. The equilibrium size of $\langle R_h \rangle$ for the micelles in $scCO_2$ was about 6 nm and the blockcopolymer-$scCO_2$ system showed the same tendency of the breaking-up of micelles with increasing pressure. It is important to add that the values of $R_g/\langle R_h \rangle$ which reflects the compactness of the spherical micelles formed in the solution is about 0.5, indicating a looser micelle configuration of THPMA-b-F7MA block copolymer chain in $scCO_2$.

In conclusion, a high pressure cell has been designed for simultaneous synchrotron small-angle x-ray scattering and laser light scattering. The cell is compact, has the same scattering volume for both scattering techniques, and can be aligned easily for synchrotron x-ray and laser light scattering measurements. This cell will be valuable to investigate structures of wide range of length scale from nanometers to microns in supercritical carbon dioxide.